Activation of the Anionic Polymerization of Styrene by Crown Tertiary Amines in Cyclohexane

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SUMMARY

The half life time of active species propagating the anionic polymerization of styrene in the presence of tetramethyltetraaza-cyclotetradecane (TMTCT), is higher than the polymerization time at room temperature. The kinetic study of the propagation step measures the activating effect for a ratio $\frac{[TMTCT]}{[PSLi]} = 1$ at room temperature. First-order kinetics with respect to living centres is observed ; the corresponding absolute rate constant is equal to $750 \ 1. \ \text{mole}^{-1}.s^{-1}$ at 20°C. Such an increase of the reactivity of ion-pairs is interpreted in terms of the stretching of the carbon-metal bond in polystyryllithium.

INTRODUCTION

The addition of complexing agents to lithium salts of carbanionic species produced by the anionic polymerization of ethylenic monomers, generally increases their overall reactivity. Nevertheless, in the case of oxygen-containing ligands, the important increase of the intrinsic reactivity of ion-pairs leads to the breaking of the C-O bond and the formation of alcoholates incapable of propagating the polymerization.

The replacement of these ligands by complexing agents exclusively containing nitrogen, leads to active species relatively stable in time, even for strongly reactive species like lithium alkyls. In this way, LANGER (LANGER 1965) succeeded in activating

the anionic propagation of ethylene by addition of TMEDA.

In a study carried out on a system analogous to the previous one, we have found that, with TMEDA, the overall activation is due to the disruption of the aggregation of ion-pairs, but that complexed non-aggregated ion-pairs are less reactive than non-complexed non-aggregated ion-pairs. We think that this relative lowering of the intrinsic reactivity of the complexed carbanionic ion-pairs, is due to vacant sites on Li^+ cation being occupied by the lone electron-pairs of the two nitrogen atoms. Such complexation by the diamine molecule prevents a possible coordination of the monomer molecule prior to its insertion in the polymer chain. In other words, the tertiary polyamine prevents electrophilic assistance by the cation. The external solvation of ion-pairs by TMEDA, hardly affects the interionic distance. So the lowering of the reactivity of ion-pairs by this complexation is not compensated for by a stretching of the C-Li bond.

By replacement of bidentate ligands like TMEDA, by crowns or by cryptands, ligand separated ion-pairs, whose reactivity is much higher than that of tight ion-pairs, may be obtained. (BOILEAU et al. 1974). In order to limit the termination reactions leading to alcoholates, we chose to study the activation effect on the reactivity of polystyryl-lithium ion-pairs, of a cyclic tertiary tetramine, viz. tetramethyltetraazacyclotetra-decane (TMTCT), which is much less readily attacked by carbanions.
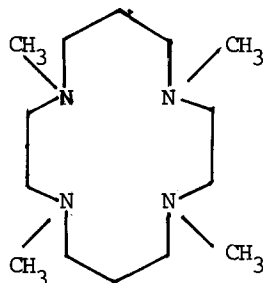
EXPERIMENTAL

- In view of the extremely high purity of the medium required in this type of polymerization system, all experiments

were carried out in all-sealed glass apparatus, under high
vacuum.

- Purification of reagents : after careful fractionnation,
cyclohexane and styrene were dried over calcium hydride, on
several sodium mirrors and finally on polystyryllithium.

- TMTCT (Strem) was purified by sublimation under high
vacuum.

- The seeds of PS^-, Li^+ ($\bar{Mn} \simeq 5.10^3$) were prepared from
tert-BuLi, following the procedure previously described (ROOVERS
and BYWATER 1975).

- The stability of active species in the presence of TMTCT
was studied by UV-Vis spectrophotometry in a vessel similar to
that described by FAVIER (FAVIER et al. 1974).

- The kinetic studies were carried out using a calorimetric
method similar to that used by CHERADAME (CHERADAME et al. 1968).
Prior to polymerization all traces of impurities were removed by
rinsing the walls of the calorimeter with a solution of carba-
nions. Such a procedure is necessary for measurements carried out
at low concentrations of active centres. After breaking a bulb
containing TMTCT and styrene in cyclohexane, in a solution of
previously prepared polystyryllithium seeds, the measurement of
the variation of temperature permitted us to follow the fast
conversion of monomer into polymer ($t_{1/2}$ from 2,4 seconds to
17 seconds. $\Delta T \sim 0,7°C$).

RESULTS AND DISCUSSION

Before studying the kinetics of the anionic polymerization
of styrene in the presence of TMTCT, we checked that the half-
life time of the active centres propagating the polymerization
exceeds the time required for polymerization at a value of
$R = \dfrac{[TMTCT]}{[PS^-Li^+]} = 1$, by following the variation of the optical den-

sity at 345 nm. Indeed, the addition of the complexing agent produces a bathochromic shift from 326 nm (λ_{max} of polystyrylli-thium in pure cyclohexane) to 345 nm, revealing a change in the structure of the ion-pairs. Table I shows that the stability of living centres at room temperature is relatively low but we shall see that this life time is longer than the polymerization half-life. Therefore, the kinetic characteristics inherent to the anionic polymerization are preserved throughout the reaction.

TABLE 1

Half-life time of polystyryllithium complexed by TMTCT.

T °C	$[SLi] ml^{-1} \times 10^4$	R	$t_{1/2}$ s
10	1.0	1	420
/	4.9	1	960
/	11	1	1500
/	11	2	1500
20	14	1	360
/	1.0	1	120

We also studied the influence of the ratio R upon the reactivity of the system. At constant concentration of active centres, we carried out experiments at different values of R. Data represented in fig. 1 show a linear variation of $\frac{V_p}{[M]}$ as a function of R for R < 1 and a constant value of $\frac{V_p}{[M]}$ for R ⩾ 1.
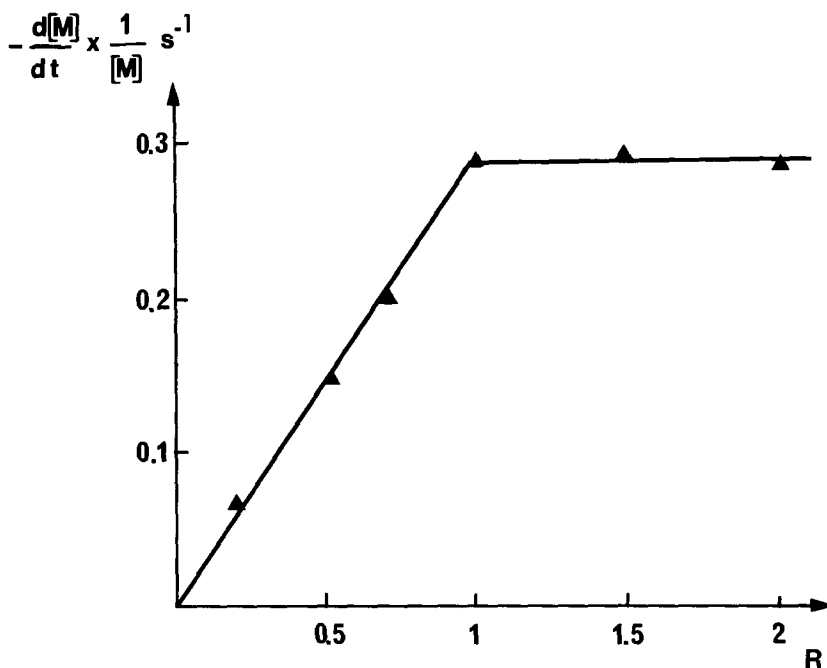
$$-\frac{d[M]}{dt} \times \frac{1}{[M]} \ s^{-1}$$

Fig. 1 : Influence of the ratio $R \ \frac{[TMTCT]}{[SLi]}$ upon the rate of polymerization at 20°C. $[S \ Li] = 3,6 \times 10^{-4}$ mole.1^{-1}.

From this result we can deduce that the addition of TMTCT to polystyryllithium gives a 1/1 complex whose reactivity is much higher than that of the non-complexed species. The equilibrium of solvation by TMTCT is strongly displaced in favor of the complexed species. In order to confirm the nature of these complexed species, we determined the kinetic order of the propagation reaction, with respect to the concentration in active centres. Plotting $\log \frac{v_p}{[M]}$ vs $\log [SLi]$ for $R = 1$ yields a straight line (fig. 2), the slope of which corresponds to a kinetic order equal to one. This result indicates that the true active species are present in a predominant concentration in the system.
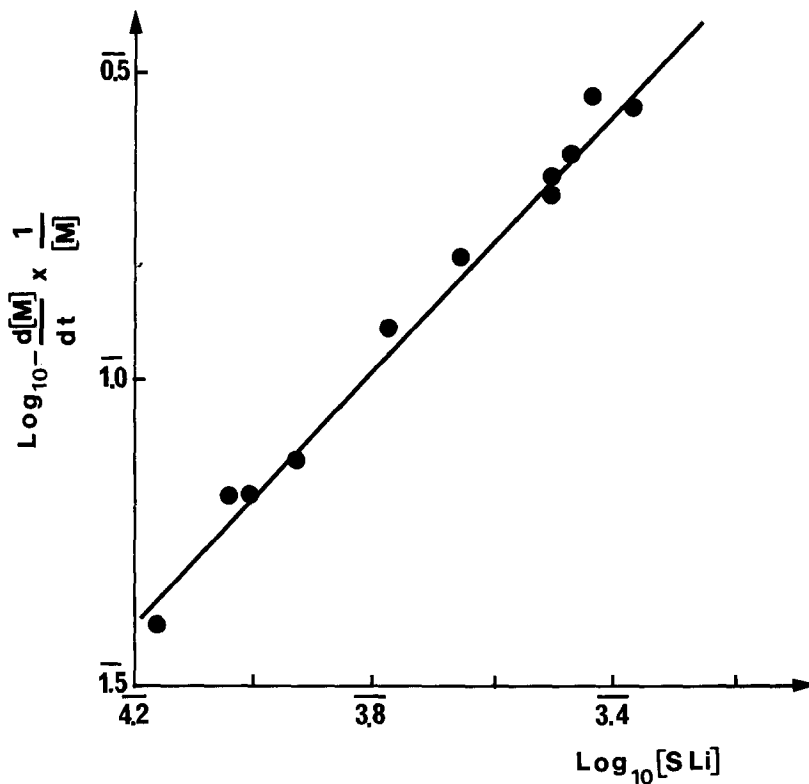
Fig. 2 : Determination of the kinetic order of the propagation step with respect to the concentration in active centres for $R = [TMTCT]/[SLi] = 1 \cdot (\frac{1}{[M]} \times d[M]/dt$ in $sec^{1})$.

It is reasonable to consider that such species are not aggregated. Indeed, as we found previously (HELARY and FONTANILLE 1978), TMEDA produces the disruption of the aggregation of polystyryllithium in non-polar solvents. Due to its steric hindrance, the effect of TMTCT should be at least as high as that of TMEDA.

The rate constant we measured is an absolute rate constant equal to 750 1. mole^{-1}. s^{-1} at 20°C.

This value is much higher than the one we determined for

ion-pairs complexed by TMEDA (k_p = 0,13 1.mole^{-1}.s^{-1}) (HELARY and FONTANILLE 1978) and much lower than that estimated of solvent-separated ion-pairs ($kp\,/\!\!/^{\pm}$ = 30 000 1.mole^{-1}.s^{-1}) by SZWARC and coll. (SHIMOMURA et al. 1967). It seems therefore plausible to admit that due to its geometry, TMTCT produces only a stretching of the -C-Li bond, with an increase in ionicity, but without true separation of charges by the tetramine.

On the other hand, the dielectric constant of the solvent may play an important role in determining the amount of stretching.

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